сообщения
объединенного
института
ядерных
исследований
дубна

E18-89-794

G.Andrassy, T.I.Mamonova

STABILITY OF PORE SIZE IN NUCLEAR TRACK MEMBRANES

1989

Nuclear Track Membranes

Nuclear track membranes are produced by irradiating of polymer films with heavy ions and a following etching of the resulted tracks. Because of this technology this kind of membranes has cylindrical pores of equal size. Pore radius can be varied in a wide range by the choice of the etching conditions. Commercial nuclear track membranes have a porosity of 8-15% and pore diameters from 0.03 up to 10 μm. In principle it is possible also to produce membranes with smaller pores, but in this case it is necessary to examine the stability of these pores.

Experiment

Polyethylene terephthalate films (thickness of 10 and 8 μm) were irradiated, respectively, with ^{129}Xe ions (124 MeV), ^{79}Br ions (40 MeV). The track densities were $6.5 \cdot 10^5$ /cm^2 and $2.0 \cdot 10^9$ /cm^2.

After a chemical treatment to increase the etching rate along the track/1/, the examples were etched. The pore size was controlled by electrical conductance measurements in the etching agent or in 1n KCl solution with pH 2.

Etching Process

Most examples were etched in 0.2n NaOH at a temperature of 70° C after chemical sensitization/1/. The first examples were placed between two half-cells filled with etching agent and the growth of the pores was controlled by electrical conductance measurements/2/. The etching curve (see fig. 1) allows to etch membranes with a known pore radius outside the cells. In a few cases the etching process in 0.2 or 0.5n NaOH at 70° C was interrupted after 3, 5, or 10 minutes and continued in 5n NaOH either immediately (see fig. 3d) or after drying the examples in the air at room temperature for 7 days (see fig. 3c).

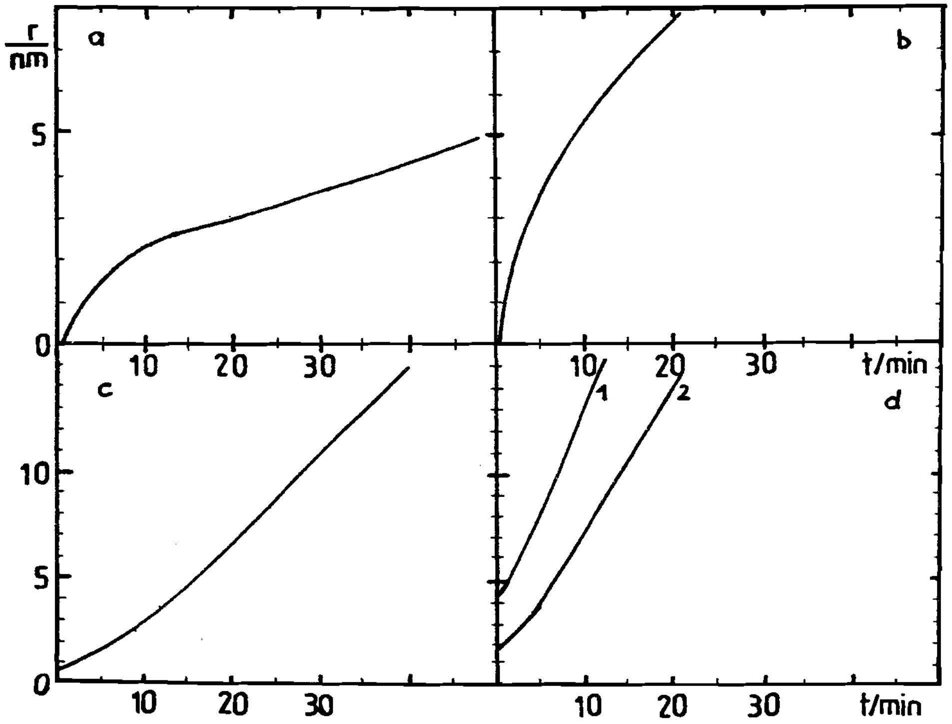

Fig. 1. Etching curves of PET membranes, d = 10 μm, irradiated with ^{129}Xe (124 MeV), N = 6.4·10^5 /cm^2; r-pore radius, t-etching time: a — 0.2n NaOH, 70°C; b — 0.5n NaOH, 70°C; c — 5n NaOH, 22°C, after 5 or 10 minutes etching in 0.2n NaOH and drying for 7 days; d — 5n NaOH, 22°C immediately after 1 — 10 min, 2 — 5 min etching in 0.5n NaOH at 70°C.

Drying Process in the Air at Room Temperature

Membranes were dryed in the air at room temperature after the etching process. As shown in fig. 2, a pore size decrease takes place depending on the pore size after etching and can lead to a complete disappearance of the pores if the initial radius was small enough.

Influence of the Medium and the Temperature of Storage on the Change in Pore Size

The membranes were stored at a temperature of 70°C in the air (1h), in distilled water (1h), and in dimethylformamide (2 min). Then they were dryed in the air at room temperature. The pore radius was measured after etching, after heating, and during the drying process. The resulting differences

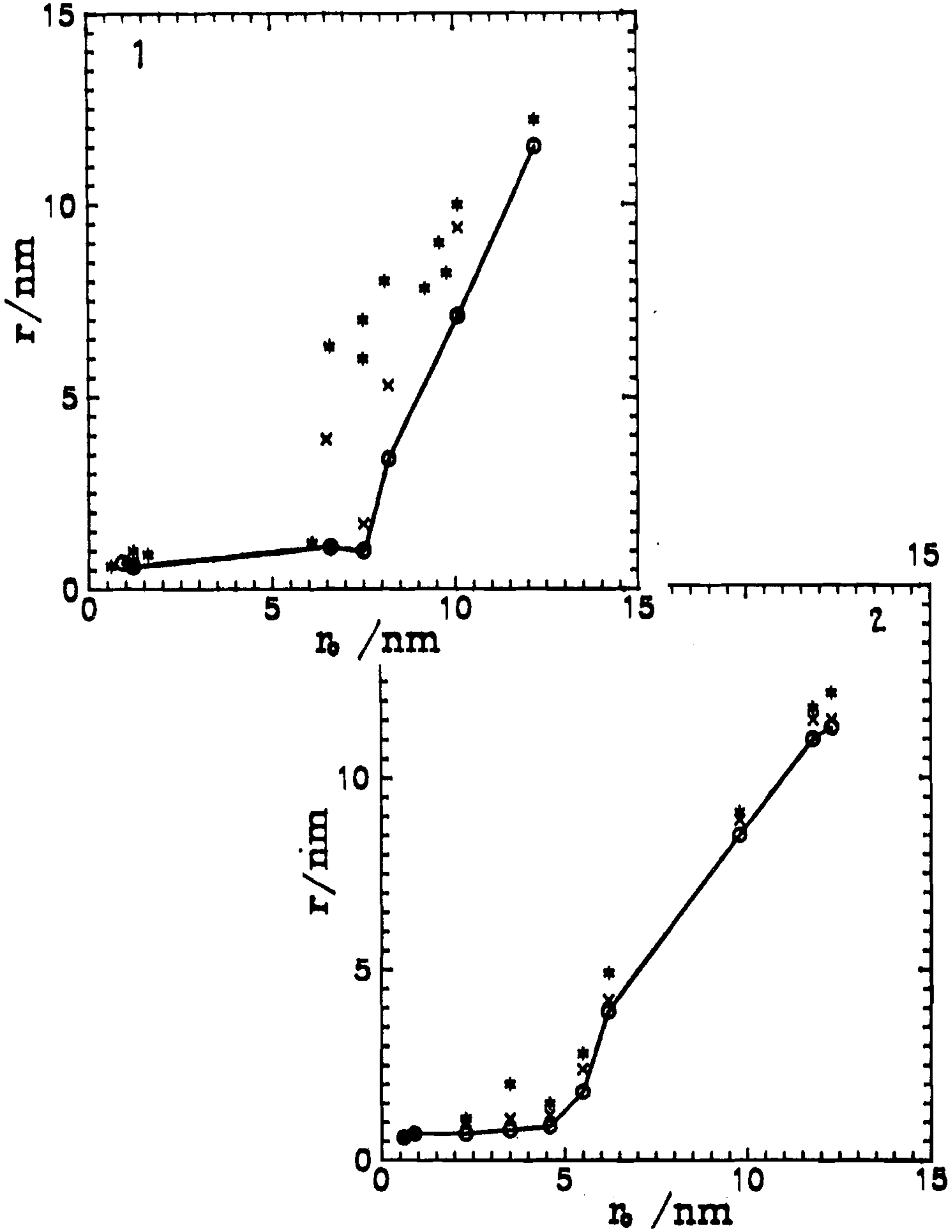

Fig.2. Drying process in the air at room temperature r — radius after etching, * — radius after 3h, x — radius after 24h, o — radius after 4 weeks. 1 — PET, d = 10 μm, N = 6.4·10^5 /cm^2, 2 — PET, d = 8 μm, N = 2.0·10^9 /cm^2.

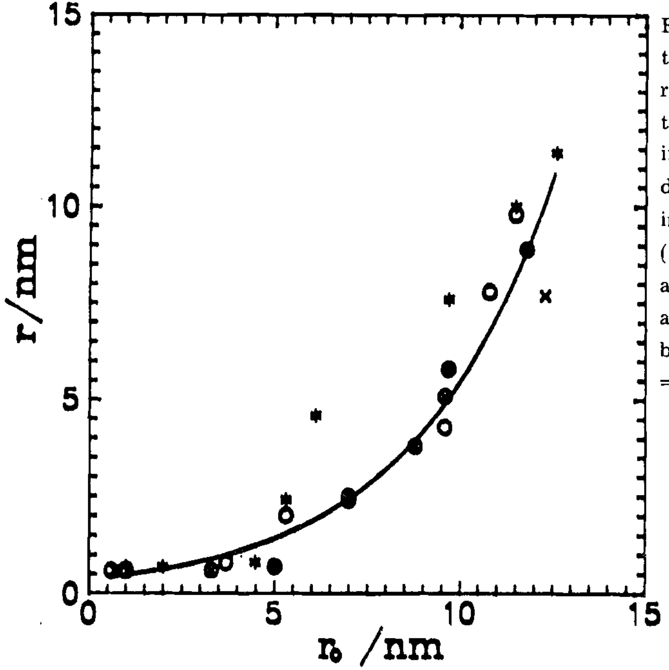

Fig.3. Drying process in the air at room temperature after storing at a temperature of 70°C o — in the air (1h), × — in dist. water (1h), * — in dimethylformamide (2 min), r_0 — radius after etching, r — radius after 4 week drying. Membrane: PET, d = 8 μm, N = = $2 \cdot 10^9$ /cm^2.

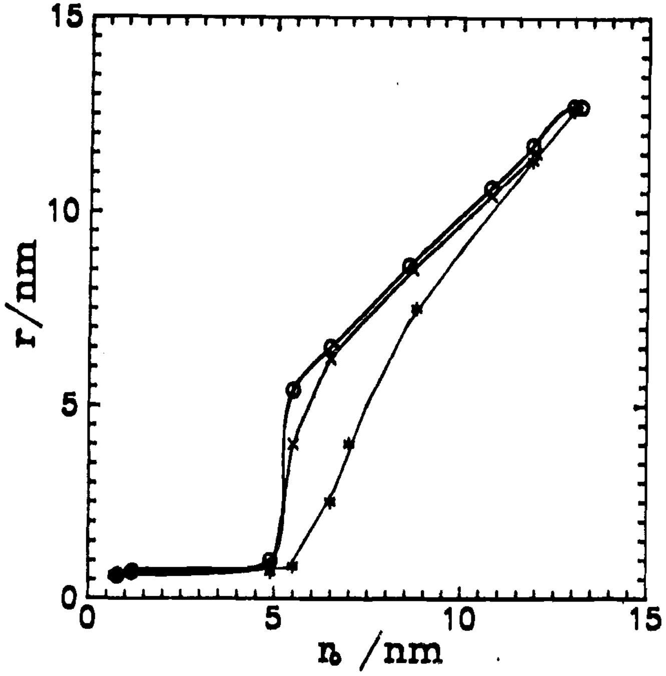

Fig.4. Drying process in the air at room temperature after treatment with * — distilled water, × — acetone, o — dimethylformamide, r_0 — radius after etching, r — radius after 4 weeks. Membrane: PET, d = 10 μm, N = $6.4 \cdot 10^5$ /cm^2.

between the pore radius after etching and after drying for 10 days are shown in fig.3. In the case of water treatment and treatment with dimethylformamide the decrease of pore radius essentially takes place during the drying process. The decrease of pore size in the membranes heated in the air is finished some hours after heating.

Influence of the Treatment with Organic Solvents after Etching on the Change in Pore Size

In some references the authors propose that the decrease of the pore size in nuclear track membranes is a consequence of capillary forces, resulting from the evaporation of the capillary liquid/3,4/. That means, that the pore size decrease should be a function of the surface tension of the liquid in the pores. In order to check this proposition some membranes were washed with acetone, dimethylformamide or distilled water after etching. Then they were dryed in the air at room temperature. The results of the measurements of the pore size after etching and after drying are shown in fig.4. Five minutes after washing with dimethylformamide the pores appeared a little bigger than after etching. After drying the membranes washed with acetone or dimethylformamide had bigger pore diameters than the membranes washed with water. If, however, these membranes come into contact with water, the process of pore size decrease also takes place as is shown in fig.4. A visible difference between the membranes washed with acetone and dimethylformamide was not found, although the surface tension of acetone is bigger than that of dimethylformamide.

Influence of the Etching Conditions on the Pore Size Change

In fig.5 the pore size decrease during the drying process in the air at room temperature after a two-step-etching is shown. There was an interruption of 7 days between the first and the second etching process. During this time the pores completely disappeared (see. fig.1a and c). In the second etching process the pores do not achieve exactly the shape of a cylinder but a little cone. This might be the reason for the stability of the pores during the following drying (see fig.5)/5/. If the etching process in 0.5n NaOH at 70°C is stopped after 3 or 5 minutes and immediately continued in 5n NaOH at 22°C, the initial pores grow and stay cylindrically. The decrease of pore size during the drying process is comparable with that in membranes which were continuously etched (see fig.6).

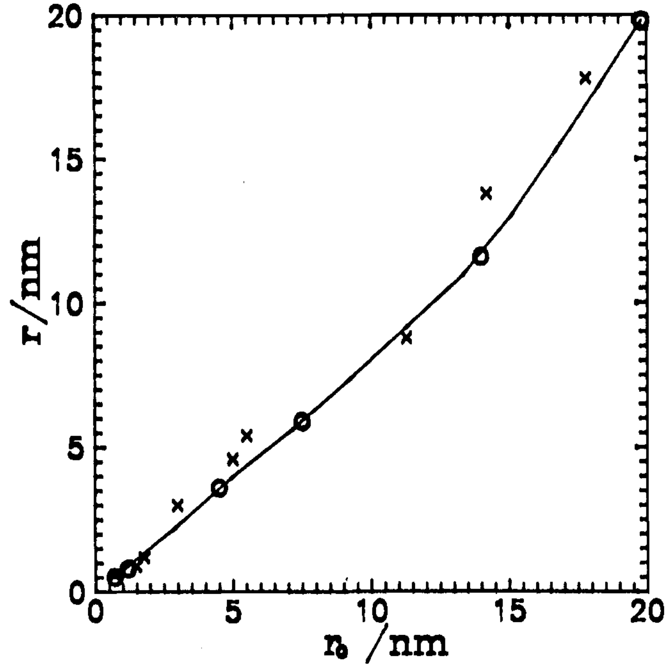

Fig.5. Drying process in the air at room temperature after a two step etching with an interruption of 7 days. Etching process see in fig.1a and c. r_o — radius after the second etching process, r — radius after 4 weeks. Membrane: PET, d = = 10 μm, $N=6.4 \cdot 10^5$ /cm^2.

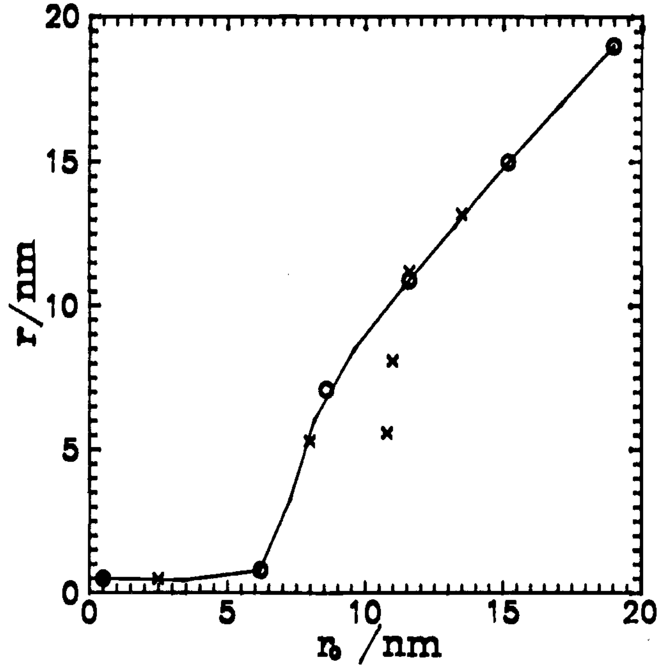

Fig.6. Drying process in the air at room temperature after a two step etching. Etching process see fig.1b and d. r_o — radius after the second etching process, r — radius after 4 weeks. Membrane: PET, d = 10 μm, $N = 6.4 \cdot 10^5$ /cm^2.

Conclusions

The results of all our studies have shown that pores in nuclear track membranes can change their size after etching, when the pore radius is very small. A visible difference between pore size after etching and after drying for some days was found when the radius after etching was smaller than 15 nm. This decrease can lead to a complete disappearance of the pores when the pore radius after etching was smaller than a critical radius. This critical radius depends on the initial material of the membranes. The time to obtain a stable pore size is the faster the smaller is the radius after etching. The dimensions and the velocity of the pore size decrease may be influenced by the temperature and the medium of storage. Principally all conditions promoting an increase of the mobility of the polymer chains also promote the decrease of pore size which should be a result of relaxation processes in the polymer to reduce the inner tensions arising from the polymer film production. In our experiments the polymer material was in the glass state. But these conclusions essentially agree with the results of similar investigation of nuclear track membranes from PET in the high-viscoelastic state/6/.

References

1. *DD-PS 235 923 A1.*
2. *Andrassy G., Mamonova T.I. – JINR Preprint 18-88-266, Dubna, 1988.*
3. *Lavrentovich Ja.I., Vypiraylenko V.A. – Kolloidnyj Zhurnal, 1987, 49, p.474.*
4. *Apel P.Ju., Kuznetsov V.I., Ovchinnikov V.V. – Kolloidnyj Zhurnal, 1987, 49, p.537.*
5. *Lavrentovich Ja.I. – Teor. i Experim. Khimija, 1987, p.569.*
6. *Ovchinnikov V.V., Seleznev V.D., Kuznetsov V.I., Kravetz L.I., Akinschin D.V. – JINR Preprint 18-87-637, Dubna, 1987.*

Received by Publishing Department
on November 24, 1989.